Research Article

Effect of Addition of Boric Acid and Borax on Fire-Retardant and Mechanical Properties of Urea Formaldehyde Saw Dust Composites

Zenat A. Nagieb, Mona A. Nassar, and Magda G. El-Meligy

1 Cellulose and Paper Department, National Research Center, Dokki 12622, Cairo, Egypt
2 Packaging and Packing Department, National Research Center, Dokki 12622, Cairo, Egypt

Correspondence should be addressed to Mona A. Nassar, monanassar65@yahoo.com

Received 12 June 2011; Revised 27 August 2011; Accepted 28 August 2011

Academic Editor: R. J. Linhardt

Copyright © 2011 Zenat A. Nagieb et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Properties of the flame retardant urea formaldehyde (UF) board made from saw dust fibers were investigated. Flame retardant chemicals that were evaluated include boric acid (BA) and borax (BX) which were incorporated with saw dust fibers to manufacture experimental panels. Three concentration levels, (0.5, 1, and 5%) of fire retardants and 10% urea formaldehyde resin based on oven dry fiber weight were used to manufacture experimental panels. Physical and mechanical properties including water absorption, modulus of rupture (MOR), and modulus of elasticity (MOE) were determined. The results showed that water absorption and bending strength decreased as the flame retardant increased. The highest concentration of (BA + BX) enhanced the fire retardant more than the lower ones. Scanning electron microscope and FTIR of composite panels were studied.

1. Introduction

Several biobased fibers such as wood, sisal, jute, flax, abaca, banana, oil palm, pineapple leaf, and bamboo have been studied as reinforcements for polymers. Among natural fibers, wood was the most extensively and more frequently used reinforcement for polymers. However, due to expensive manufacturing process of wood fibers, inexpensive and sustainable alternatives such as agricultural waste have attracted considerable interest [1].

Flammability of polypropylene, sawdust/rice husk-filled polypropylene composites, and flame retarding effect of magnesium hydroxide for these composites were studied by horizontal burning rate and oxygen index tests. Effect of flame retardants such as boric acid or zinc borate in combination with magnesium hydroxide was also studied. It was found that magnesium hydroxide can effectively reduce the flammability (almost 50%) of natural fiber-filled polypropylene composites. No synergetic effect was observed when magnesium hydroxide was used in combination with boric acid and zinc borate. Marginal reduction in the mechanical properties of the composites was found with addition of flame retardants [2, 3].

Fire, mechanical, and thermal properties of novel fire-retardant composites have been assessed with typical materials currently used in aerospace, such as epoxy-based materials for structural parts and phenolic-based materials for internal furnishing. These newly developed materials (neat resins and composites) present a significant improvement in their properties from 40 to 70% without loss of thermal and mechanical behavior [4]. The most successful flame retardant additives on the market today are halogenated flame retardant additives [5]. Halogenated compounds can be either physically introduced or reacted with the polymer chain. However, halogenated compounds can have negative environmental and toxicological impacts [6]. As a result of this environmental concern, flame retardant boron compounds are one of the safest in current use, and no or other harmful effects have occurred due to this or other industrial uses [7].

Boron compounds have long been used as fungicides and insecticides for wood preservation and are especially effective
against termites. Boron-based buffers have also been used as additives in fire-retardant treatments and have been found to significantly reduce the severity of thermal degradation [8, 9]. Boron compounds reduce the flame spread of wood but may have diverse effects on hygroscopicity. Wood treated with inorganic flame-retardant salts is usually more hygroscopic than untreated wood, particularly at high relative humidity. Increases in the equilibrium moisture content of such treated wood will depend upon the type of chemical, level of chemical retention, and size and species of the wood involved [10].

The objective of this work was to study the effect of using the safety inorganic boron compounds on fire retardance and other properties of composite board made from saw dust, urea formaldehyde, and paraffin wax as a petroleum-based product.

2. Materials and Methods

Saw dust was used as a source of wood fiber. It was soaked first in sodium hydroxide solution (2%) at 50°C for 1 h, where sodium hydroxide treatment is mainly a process of surface activation. After the desired time, it was washed with warm water (50°C), then pressed to release the water, and left to dry in an air oven at 50°C to reduce the moisture content to about 13%. The pretreated sawdust was then granulated using a Retsch GmbH 5657 HAAN (West Germany) having a 3 mm screen.

Commercial urea formaldehyde binder with a solid content of 55% was used with the ratio of 10% w/w based on the oven dry weight of the saw dust particles.

Boron was added to the UF as boric acid (BA) and borax (BX) at final concentration of 0.5, 1, and 5% (w/v) and a mixture of 5:1 (BA: BX, w/w) with the same concentration levels. The glue was catalyzed by adding ammonium chloride as hardener (solid content 33%) at 1% (based on glue weight) and fine particles of paraffin wax as hydrophobic substance (PW) were also added to the glue. Pressing for manufacturing of board was occurred at 50 KN, 150°C for 5 min to the required thickness. Modulus of rupture (MOR) and modulus of elasticity (MOE) were calculated on the basis of initial sample dimensions. Five specimens were tested per sample, and the mean values were recorded.

Also, the sawdust composite board was tested for water absorption according to ASTM D-570–81 [11] in which the samples were immersed in boiling water for 2 h and room temperature water for 24 h and 7 days. After excess water drained off, the weights were measured. The following equation was applied:

\[
\text{Water absorbivity} \% = \frac{W_w - W_i}{W_i} \times 100, \quad (1)
\]

where \(W_i\) is the initial weight and \(W_w\) is the wet weight.

2.1. Testing of Fire Retardancy. A number of panels were tested according to the Japanese Industrial Standard JISA 1322 (1982) [12]. 15 cm long and 3 cm wide and 0.8 cm thick board panels were clamped with steel holders and exposed to the heating flame at an angle of 45 degree. Benzene flame was used as the heat source. The heating flame was adjusted to a height of 7 cm and was applied for 10 min, based on preliminary tests in which the flame penetrated the other surface of the control panels. The times for the panels to be charred and ignited were recorded. The postflaming time was recorded. Flam penetration through the board, weight loss due to consumption, and char length were determined.

2.2. Scanning Electron Microscopy. Scanning electron microscopy SEM of fractured surfaces of composite test specimen was calculated on JEDL JEM-100 S electron microscope using the gold.

2.3. Infrared Spectra. The infrared spectra for treated and untreated saw dust fiber were measured by using Jocc FTIR spectrophotometer apparatus, Japan. The samples were measured as KBr discs.

3. Results and Discussions

3.1. Mechanical Properties and Water Absorption. Based on TSEN 312 standard, 11.5 N/mm² is the minimum requirement for MOR of particleboard panels for general uses [13]. Panel type 1 (control) had higher MOR than the general-purpose requirements. The results of the mechanical properties in case of adding flame retardant chemicals are presented in Table 1. A lower level of fire retardant (0.5%) seems to increase the MOR and MOE. However, subsequent increment reduced the MOR and MOE significantly. MOR of treated samples normally decreased as percent of flame retardant chemicals was increased. This probably could be due to the presence of the flame-retardant chemicals depositing on the fibers of the boards as indicated by the SEM work (Figure 1), or it may be due to the degradation of cellulose fiber by the flame retardants [14].

Urea formaldehyde is not a waterproof binder, and it absorbs moisture when exposed to severe moist conditions. When the board was immersed in water, swelling took place because of particle hygroscopicity, spring back (the release of built-in compressive forces brought about during manufacture), and water absorption affinity of the binding material. After 24 h of soaking the water absorption value increased to 80%.

Table 1 also shows the effect of boron compounds on water absorption from 1 to 7 days under room temperature and for 2 hours on boiling water. This treatment makes the water absorption decrease and reach the lowest value after 24 hours (55.2)%). Also it was found that the presence of boron compounds decreases water absorption by 50–80% for different samples. The explanation of the improvement of water resistance is attributed to cellulose structure of the lingo cellulosic raw material, since a cellulose molecule contains three available hydroxyl groups that are responsible for its hydrophilic nature [15]. Boron addition may accelerate and achieve maximum cross-linking between UF-adhesive and available hydroxyl groups of lingo cellulosic material and hence reduce the number of hydroxyl groups in both lingo.
Table 1: Mechanical properties and water absorption of modified saw dust composite.

<table>
<thead>
<tr>
<th>Different modification samples</th>
<th>Mechanical properties</th>
<th>Water absorption after immersion in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bending strength (N/mm²)</td>
<td>MOE (N/mm²)</td>
</tr>
<tr>
<td>Saw dust + urea formaldehyde (control)</td>
<td>12.5</td>
<td>1161.4</td>
</tr>
<tr>
<td>Saw dust + UF + paraffin wax</td>
<td>8.2</td>
<td>982.9</td>
</tr>
<tr>
<td>Saw dust + UF + P.W + 0.5% (BA + BX)</td>
<td>7.6</td>
<td>948.6</td>
</tr>
<tr>
<td>Saw dust + UF + P.W + 1% (BA + BX)</td>
<td>7</td>
<td>902</td>
</tr>
<tr>
<td>Saw dust + UF + P.W + 5% (BA + BX)</td>
<td>5.049</td>
<td>863.5</td>
</tr>
</tbody>
</table>

Table 2: Infrared assignments for absorption peaks of sawdust wood modified by urea formaldehyde and different concentrations of (BA + BX).

<table>
<thead>
<tr>
<th>wave number (cm⁻¹)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3500–3300</td>
<td>O–H stretching</td>
</tr>
<tr>
<td>2800–3000</td>
<td>C–H stretching in methyl and methylene groups</td>
</tr>
<tr>
<td>2920, 2850</td>
<td>Aliphatic CH₂ asymmetric stretch</td>
</tr>
<tr>
<td>1750–1730</td>
<td>C=O stretching in carbonyl</td>
</tr>
<tr>
<td>1640–1618</td>
<td>C=C alkenes</td>
</tr>
<tr>
<td>1510–1504</td>
<td>C=C aromatic skeletal vibrations</td>
</tr>
<tr>
<td>1462–1425</td>
<td>CH₃ lignin</td>
</tr>
<tr>
<td>1384–1350</td>
<td>Phenol–borate B–O</td>
</tr>
<tr>
<td>1260–1234</td>
<td>C–O stretching vibration in lignin and hemicelluloses'</td>
</tr>
<tr>
<td>1170–1153</td>
<td>C–O–C asymmetric bond</td>
</tr>
<tr>
<td>756</td>
<td>Out-of-plane ring deformation</td>
</tr>
<tr>
<td>691</td>
<td>COH out-of-plane ring bending</td>
</tr>
</tbody>
</table>

cellulosic components and UF-adhesive. This causes the reduction of hydrogen bond formation with water molecules during soaking. Besides, cross-linking of OH groups of lingo cellulosic fibers with free HCHO contains –O–C–O–bonds. Therefore, hydrogen bonding and wet-ability greatly decreases, and consequently, water repellency increases [16].

Furthermore, paraffin wax enhances water absorption but not too much as boron compound does, since water absorption reaches 70.2 after 24 hours. Addition of boron compounds to paraffin wax gives an excellent water-repellent surface which is rendered a hydrophobic surface towards composites.

3.2. Scanning Electron Microscopy. It is clear from Figure 1(a) that micrograph shows a very irregular surface. There are some holes and some depressions where fibrous particles are missing probably because debonding occurred.

SEM of saw dust + urea formaldehyde (Figure 1(b)) shows a more compact structure than that of the saw dust fibers (Figure 1(a)); the fibers have flattened and are spreading out. This indicates that thermoplasticity has been achieved [17]. One can see that fibrils are stretched because a good interaction occurred, and fibrils were split in 2 parts, that is, the crack runs inside wood, and not at the interface cohesive features of the nature which one usually finds in systems showing good adhesion.

Electron microscope image of wood + 10% urea formaldehyde + paraffin wax + composite shows that wax changed the macroscopic visual aspects of the fibers. As the paraffin waxes incorporated the microfibers, the tendency to aggregation increased due to an increase in their chemical affinity as shown in Figure 1(c). Moreover, increasing the percentage of addition of boron compound leads to changing composite into a remarkably plastic-like material as shown in Figures 1(d), 1(e), and 1(f). Addition of boron compound helps optimal macromolecules compound in creating water-repellent composite surfaces comparable to those made from organ-silicon macromolecules compounds [18].

3.3. FTIR Spectroscopic Analysis of Modified Saw Dust Wood Composite. The efficiency of the chemical treatment was investigated by FTIR spectroscopy as shown in Table 2 [19, 20].

Figure 2(a) illustrates the absorption bands of sawdust wood treated with urea formaldehyde. It shows a strong absorption band at 3389 cm. This band is broad and typical of hydrogen-bonded NH and OH [21]. Also the appearance of sharp peak in region 2600–2190 cm is due to the possibility of the presence of primary and secondary amides.

Figure 2(b) shows the absorption of sawdust treated with 10% urea formaldehyde + paraffin wax. It shows a slight difference between two spectrums. Figure 3 shows c-modified sawdust wood treated with 0.5% (BA + BX), d-modified sawdust wood treated with 1% (BA + BX), and e-modified sawdust wood treated with 5% (BA + BX). It is clear from Figure 3 that the more the concentration of (BA + BX), the more the intensity of the B–O band at 1310–1350 cm. Moreover, the absorption band at 1734–1745 cm due to carbonyl group of boric acid increased the intensity, as the concentrations of (BA + BX) increase from 0.5% to 5%.

3.4. Flame Retardation of Modified Saw Dust Composite. The fire-retardant treatment of wood products manufactured by pressing is easy to be implemented by adding the fire-retardant to raw materials before the pressing phase. The most common example of such products is fire retarded particle board.
Figure 1: Scanning electron microscopy of (a) saw dust wood, (b) wood + 10% urea formaldehyde, (c) wood + 10% urea formaldehyde + paraffin wax, (d) wood + 10% urea formaldehyde + paraffin wax + 0.5%, (BA + BX), (e) wood + 10% urea formaldehyde + paraffin wax + 1% (BA + BX), and (f) wood + 10% urea formaldehyde + paraffin wax + 5% (BA + BX).
Figure 2: (a) FTIR spectra of sawdust treated with urea formaldehyde. (b) FTIR spectra of sawdust treated with urea formaldehyde + paraffin wax.

Figure 3: (c) FTIR spectra of sawdust treated with urea formaldehyde + paraffin wax + 0.5% (BA + BX). (d) FTIR spectra of sawdust treated with urea formaldehyde + paraffin wax + 1% (BA + BX). (e) FTIR spectra of sawdust treated with urea formaldehyde + paraffin wax + 5% (BA + BX).

It is clear from Table 3 that the addition of 0.5% (BA + BX) to urea formaldehyde composite enhances the reduction glowing time to half from 90 sec. to 42 sec. Moreover, the weight loss reaches 67, and the char length decreases from 50 mm in case of 10% urea formaldehyde to 12 mm in case of treatment by adding 0.5% (BA + BX). In case of applying 5% (BA + BX), the char length decreases to the minimum length 2 mm. These results indicate that the addition of 5% (BA + BX) enhances flame retardation [22]. Combination of borax and boric acid continues to be used in cellulose and other hydroxyl-containing polymers. This mechanism occurs through changing the pyrolysis of wood. Ideally, the reactions would proceed so that cellulose decomposes to char and water: 

\[(C_6H_{10}O_5)n \rightarrow n(6C + 5 H_2O).\]

Water provides heat sink, fuel diluents, and a propellant for the fuel out of the flame zone. In practice, fire retardants based on this principle reduce the amount of burning pyrolysis products and thus reduce the heat released by the product.

4. Conclusion

This study indicates the suitability of sawdust for making urea formaldehyde-bonded particleboards in presence of boron compounds as flame retardant additives. Based on the results, the following conclusions were drawn.

(i) Increasing concentrations of fire retardants from 0% to 5% decreases the bending strength of finished board from 12.5 N/mm² to 5.049 N/mm².

(ii) Addition of traces of paraffin wax and boron compounds gives excellent water-repellent surface which creates a hydrophobic surface towards composites.

(iii) The addition of (BA + BX) is a good factor for good flame protection of the composite.

(iv) The ideal concentration of fire-retardant materials to attain good flame proofing is found to be 5%. Based on this, cheaper and better quality fire-resistant particleboards can be made from saw dust. These boards can be used in various ways such as in ceiling tiles, partitioning, false ceilings, and interior decorative sheets. This will prevent fire hazards in order to protect life and property if used on a large scale.

References


